Importance of 'unimportant' experimental parameters in Li–S battery development

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HIGHLIGHTS

- Elucidating complexity of parameters influencing Li–S performance.
- Systematic study of experimental parameters influencing Li–S cycling performance.
- Identification of experimental parameters having stronger and weaker or no effect.
- Parameters related to electrolyte are more important than those for composite electrode.
- Recommendations to unify reporting on Li–S system to be able to track advances in the field.

ARTICLE INFO

ABSTRACT

Lithium–sulphur batteries are among the most promising systems for the next generation of rechargeable lithium batteries. Whereas a wide range of factors contribute to the overall performance of the Li–S system, reported optimization procedures typically focus on the development of novel structured cathodes. Here, the importance of often-neglected experimental parameters contributing to the performance of Li–S systems is demonstrated. Specifically, the effects of varying the amount of electrolyte, the salt concentration and the type of electrolyte additive are presented and factors that improve cycling stability are discussed. Some of the parameters, such as sulphur-particle size and the type of conductive additive used in the electrodes, affected the cell's performance less than might be expected. Long-term cycling (up to 500 cycles) with a low amount of electrolyte is demonstrated. Our results suggest that parameters related to the electrolyte are more important for improving the overall performance than those concerning the electrode structure.

1. Introduction

The current interest in lithium–sulphur batteries is based on sulphur's high theoretical specific charge of ~ 1672 mA h g^{-1} [1]. Commercialization of Li–S batteries is hindered by several still unresolved challenges. Some of them are inherent to sulphur, in particular to its insulating nature. This means that the rate capability is low and that the active material is isolated. Therefore, substantial amounts of conductive additives are needed in order to ensure sufficient electronic contact, which in turn enables the full utilization of the active material. Other well-known and unwelcome processes include the so-called polysulphide shuttle, which leads to the accumulation of insulating deposits and thus to irreversible charge losses. The typical discharge profile in Li–S battery features two plateaus, an upper one at about 2.4 V, where sulphur is reduced to long-chain polysulphides, and a lower one at about 2.1 V, where long-chain polysulphides are reduced first to short-chain polysulphides and then to lithium sulphide. The polysulphide shuttle is caused by the high solubility of long-chain polysulphides and the fast kinetics at the upper discharge plateau, resulting in the loss of active material, its low utilization and thus in a capacity decay during cycling [1,2]. The slower kinetics of the lower discharge plateau and the low solubility of short-chain polysulphides causes deposition of an insulating layer on any accessible surface – cathode, anode, separator, etc. – which clogs the cathode structure, resulting again in a poor utilization of active material and in capacity decay [2].

Many efforts have been directed towards mitigating the difficulties that hinder the development of Li–S system, but they often offer only partial solutions. Most of the reported studies focus on finding new structured cathodes, especially conductive carbon-based hosts for sulphur. Far fewer works are found in the

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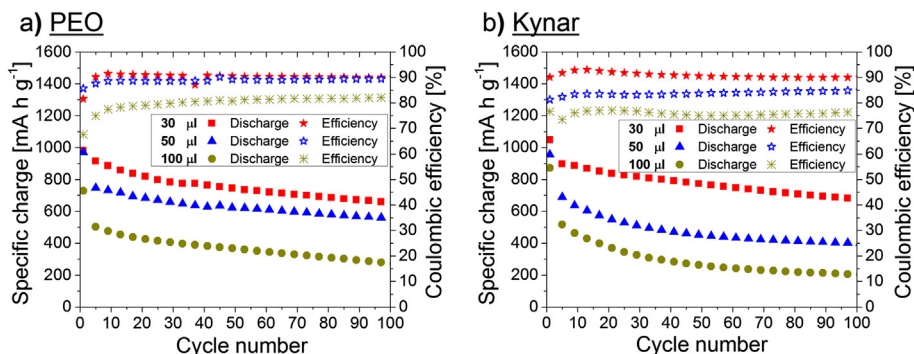 *E-mail address:* sigita.urbonaite@psi.ch (S. Urbonaite).

Fig. 1. Cycling performance of electrodes using PEO (a) and Kynar (b) as binders, with different amounts of electrolyte containing 1 M LiTFSI.

literature that report studies of the effects that different electrolyte modifications and other experimental parameters have. Many improvements have been made in the area of sulphur-host development, addressing the polysulphide shuttle and the containment of highly mobile long-chain polysulphides within carbonaceous or other structures [1,3–7]. Often, but not always, coating with polymer or inorganic materials brings improved results. But whereas such developments led to the construction of Li–S batteries with high specific charge and good cycling stability [8–10], many of these sophisticated structures do not offer better specific-charge values than electrodes based on simple carbon black. To the contrary, many advanced architectures suffer from a diminished specific charge, and demand complicated and expensive sets of procedures and the utilization of expensive and difficult-to-upscale materials, such as graphene or hierarchically ordered porous carbons [4,6,11–13].

Our approach is to study and optimize simple composites made of commercially available sulphur and carbon black. By tuning experimental parameters – such as the type of binder material [14], electrode conductive additives and electrolyte additives, as well as the amount of electrolyte – we can learn a lot about the behaviour of the Li–S system and improve its performance. This knowledge may in turn be used to achieve even better results using advanced structured-carbon hosts for sulphur. In the present work, we achieved cycling stabilities and specific-charge values equal or better than those reported for many complicated structured carbonaceous sulphur hosts [4,6,12], merely by optimizing a system with electrodes based on carbon black and made of simple, cheap and commercially available materials.

The goal of this study is to demonstrate the importance of experimental parameters, some of which are often not even specified in the experimental sections of published works, to understand their effect and thus to improve the performance of Li–S batteries.

Two types of experimental parameters were tested and their importance evaluated: those related to the electrolyte and those related to the composite electrode.

2. Experimental

Standard Li–S composite electrodes were prepared mixing 60% of sulphur (Alfa Aesar) and 30% of carbon black (Super P, Timcal, Switzerland), and using 10% of PEO (polyethylene oxide, MW = 4,000,000 g mol^{-1}, Sigma–Aldrich, Germany) as the binder prepared by dissolution in acetonitrile. For comparison, PEO was replaced in one series of tests by Kynar Flex 2801 (Solvay, Belgium) dissolved in acetone. For testing the effect of conductive additives in the electrode, part of the Super-P carbon was replaced by

graphitized carbon nanofibres (GCNF, Nanoamor, USA). To test the influence of different sulphur types, electrodes were prepared with sublimed S (STREM Chemicals, USA), refined S (Acros Organics, Belgium) and precipitated S (STREM Chemicals, USA), keeping the same component ratios. Slurries were mixed by turbostrirring, and then doctor-bladed onto carbon-pre-coated aluminium foil. After at least 24 h of drying in air at room temperature, electrode discs of 13-mm diameter were punched out and inserted into a glove box for assembly. Li–S cells were assembled in Ar atmosphere into coin-type cells by placing a 17-mm diameter Celgard 2400 (Celgard, USA) separator onto the composite electrode, introducing between 30 and 100 μl of electrolyte, which was either 1 M, 2 M or 4 M LiTFSI (lithium bis(trifluoromethane sulphone)imide) in DME (dimethoxyethane):Diox (1,3-dioxolane) in a ratio 2:1, or 1 M LiTFSI in DME:Diox (2:1) with 0.5 M LiNO$_3$ (Fluka, Germany) additive. Electrolytes with different concentrations of salts were prepared based on 1 M LiTFSI electrolyte (Novolyte, USA) by adding appropriate amount of LiTFSI (TCI, Japan) or LiNO$_3$ when electrolyte with additive was prepared. Typical loading of S was ∼1.5–2 mg cm^{-2}, depending on binder and electrode-conductive-additives used; thickness of electrodes was ∼0.080 mm, with exception of electrodes with sublimed sulphur, which due to large particle size was ∼0.150 mm.

Cells with lithium (0.75 mm thick, Alfa Aesar, USA) counter electrode were galvanostatically tested between 1.8 and 2.7 V, at different C-rates (C/5 or C/10) and for at least 100 cycles (the C-rate is defined as $I = 1672$ mA g^{-1} of S) using Astrol (Switzerland) battery cycler. Specific charges are calculated per mass of sulphur; and only the values of specific charge obtained during discharge process are reported here. For each specific set of experimental
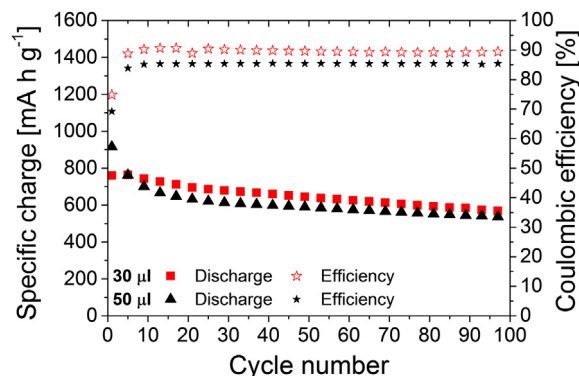

Fig. 2. Cycling performance of electrodes using a PEO–Kynar blend as a binder, tested with different amounts of electrolyte containing 1 M LiTFSI.
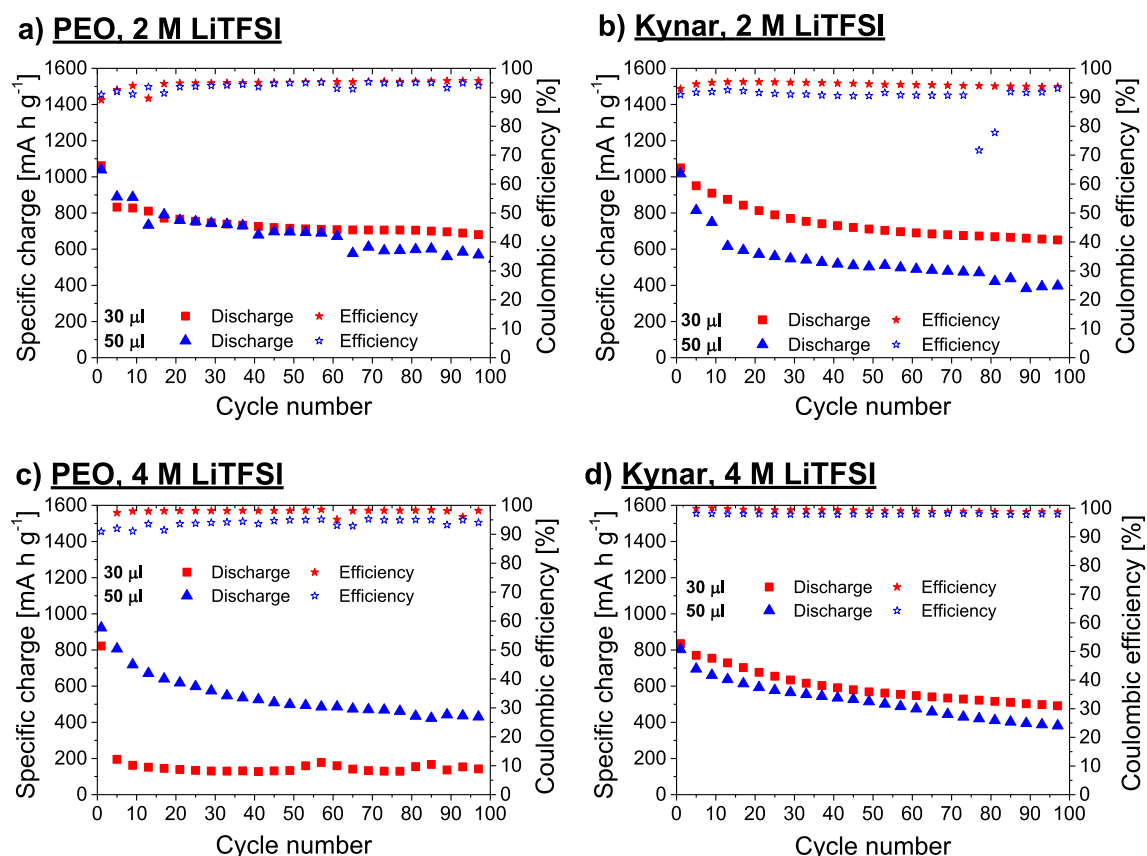
Fig. 3. Cycling performance of electrodes using PEO (a,c) and Kynar (b,d) as binders, with different amounts and concentrations of electrolyte, 2 M LiTFSI (a,b) and 4 M LiTFSI (c,d).

parameters at least two cells were tested to confirm reproducibility of the obtained results.

Morphological investigations were carried out using a scanning electron microscope (SEM) Ultra 55, Zeiss (Germany) operated at 5 kV accelerating voltage. For analysis, electrode coatings supported on carbon-coated aluminium foil were placed on SEM stubs onto adhesive conductive carbon tape.

3. Results and discussion

First, we report results mainly concerning parameters related to the electrolyte — its amount, salt concentration and presence of electrolyte additive. However, the effect of binder type, sulphur type and the presence of conductive electrode additive were also investigated in parallel and are reported in the second part of this section.

A number of cells were prepared with different amounts of electrolyte, ranging from 30 to 100 μl. In the same series of experiments, standard electrodes containing PEO as the binder and additional electrodes with Kynar instead of PEO were cycled in order to check the effect of the binder type and to see whether there are any synergetic effects. The electrodes with both types of binder had the highest practical specific charge when only 30 μl of electrolyte was used, and they retained a specific charge of $\sim$700 mA h g^{-1} after 100 cycles (see Fig. 1).

The PEO binder was superior relative to Kynar when the amount of electrolyte was increased to 50 μl; after 100 cycles, the specific charge value was at 600 mA h g^{-1} for the PEO-based electrode, while in case of Kynar it was only at 400 mA h g^{-1}. With a high electrolyte amount, 100 μl, both types of electrodes showed poor performance and after 100 cycles the specific charge dropped to

300-200 mA h g^{-1}. Also in this case, electrodes containing PEO binder exhibited slower fading and the remaining capacity after 100 cycles was slightly higher. Due to the poor performance of cells with 100 μl of electrolyte, all further experiments were carried out with only the smaller amounts of electrolyte, namely 30 and 50 μl.

Furthermore, polymer blends with both PEO and Kynar (mixed at a weight ratio of 1:1) were tested. Fig. 2 shows that in this system, there is no significant difference in practical specific charge when comparing the two amounts of electrolyte. In the case of 50 μl of electrolyte, the specific charge is higher compared to using solely Kynar as a binder, bringing it to the same level as electrodes with solely PEO (see Fig. 1). However, a smaller amount of electrolyte led to a slightly higher coulombic efficiency. Based on these results, it is
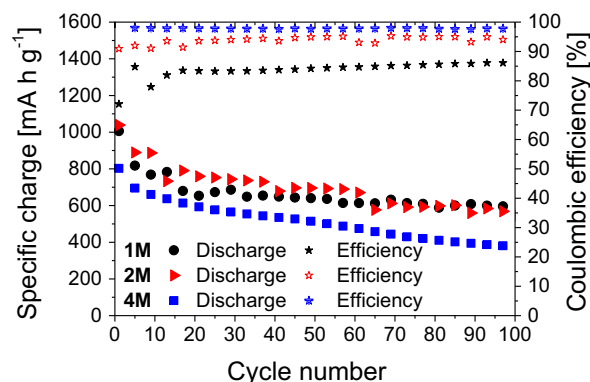

Fig. 4. Galvanostatic cycling of S—C(Super P)—PEO composite electrodes with different LiTFSI-salt concentrations and electrolyte amount of 50 μl.
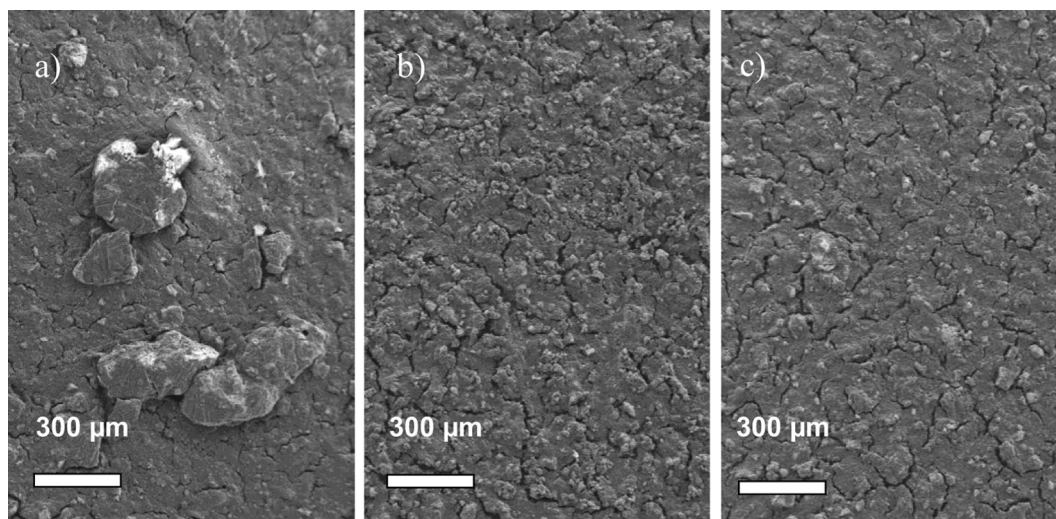
Fig. 5. SEM micrographs of sulphur–carbon composites with sublimed S (a), refined S (b) and precipitated S (c).

not possible to conclude which binder − PEO or Kynar − is better for Li−S batteries; it strongly depends on the amount of electrolyte used.

The effect of the salt concentration was investigated by preparing electrolytes with 3 different salt concentrations (1 M, 2 M and 4 M LiTFSI in DME:Dio*x*), which were tested by cycling standard electrodes at C/10. With an increase of salt concentration in the electrolyte, its viscosity increases and the ability to dissolve salt decreases. Therefore it is expected that for lithium polysulphides it becomes more difficult to be dissolved in highly concentrated electrolytes; moreover, due to higher electrolyte viscosity, the mobility of (especially long-chain) polysulphides is expected to be reduced.

In Fig. 3, a comparison between electrodes prepared with PEO and Kynar binders is presented, where the salt concentration and the amount of electrolyte was varied. When the PEO-based electrode is cycled with 2 M electrolyte, the practical specific charge does not strongly depend on the amount of electrolyte (see Fig. 3a). However, when the electrolyte concentration is increased to 4 M, the PEO-based electrode stops working with only 30 μl of electrolyte (Fig. 3c); also, the specific charge of the cell with 50 μl of electrolyte is decreased. At the same time, when cycling the Kynar-based electrode with 2 M electrolyte, a clear dependence on the amount of electrolyte is seen, and the specific charge is much lower

when 50 μl of electrolyte are introduced into the cell (Fig. 3b). When increasing the electrolyte concentration to 4 M in combination with the Kynar-based electrode, we see that the difference in specific charge attributed to different amount of electrolyte is much smaller, even if the specific charge itself is lower. It is therefore, again, difficult to say whether Kynar or PEO is the better binder, as Kynar works at higher electrolyte concentrations with lower electrolyte amount better than PEO, whereas PEO works better at lower electrolyte concentrations and with higher amounts of electrolyte, see Fig. 3. This behaviour can be explained by the ability of the various solvents [15], including electrolyte to swell PEO, thus contributing to a higher viscosity of the electrolyte at high salt concentrations and the low amounts of electrolyte in the cell. This can be the reason, why Kynar, which is not swelled by electrolyte and does not contribute to the electrolyte's viscosity, is working better as a binder in already viscous electrolyte.

Comparing the cells tested with all three salt concentrations at the same amount of electrolyte (50 μl), it can be clearly seen that both 1 M and 2 M concentrations result in the same specific charge (Fig. 4). However, the coulombic efficiency is much lower using 1 M electrolyte. With concentration of 4 M LiTFSI, the coulombic efficiency is close to 100%, but the specific charge is lower compared to when lower concentrations of electrolyte are used, and it suffers from substantial fading. Furthermore, the coulombic efficiency is
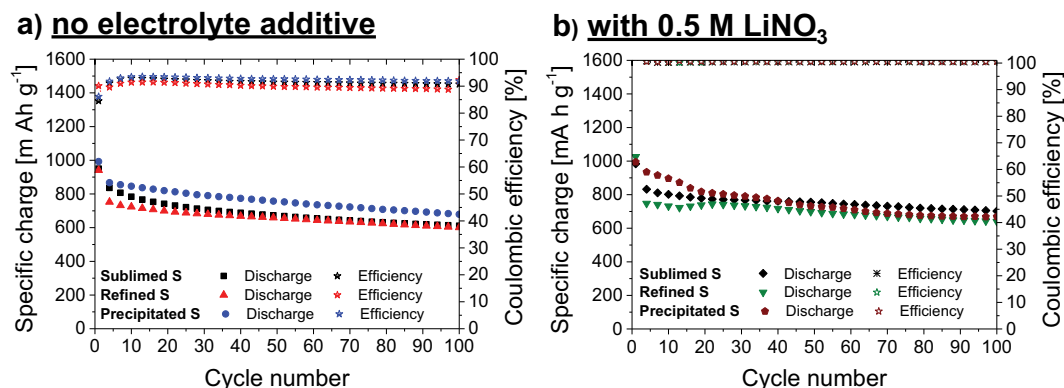

Fig. 6. Galvanostatic cycling of S−C(Super P) composite electrodes containing different types of sulphur at a rate of C/5 with 30 μl of electrolyte without additive (a) or with 0.5 M LiNO₃ (b).
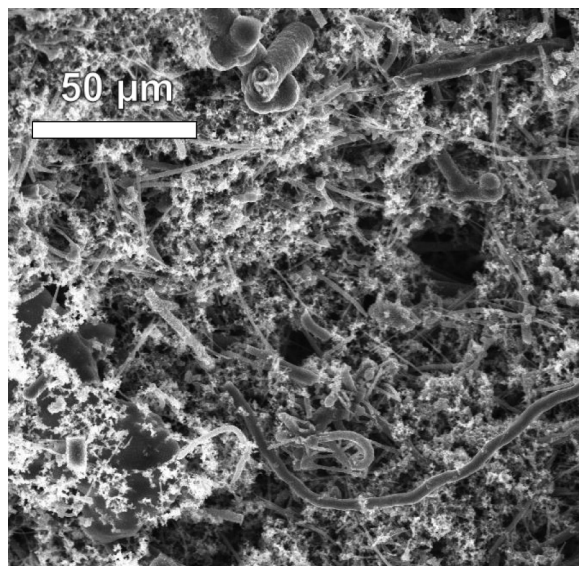
Fig. 7. SEM micrograph showing the morphology of a sulphur–carbon composite electrode, where part of Super P carbon is replaced by GCNF.

consistently higher for higher concentrations of the salt in the electrolyte. This behaviour can be attributed to the improved lithium-ion availability at higher salt concentrations, but also to the lower solubility of polysulphides in highly concentrated salt environments and to the higher viscosity of electrolyte. The observed decrease in specific charge with increased LiTFSI concentration is in contradiction to a recent study by Shin et al. [16], which most probably can be explained by differences in the preparation of the carbon–sulphur composite electrode (such as in the type of binder) or in the amount of electrolyte used, which is not indicated in their work. This discrepancy underlines the importance of reporting all experimental parameters, in order to enable comparison and understanding of the results.

Further, we explored electrode parameters, such as the sulphur type and the particle size, which have been described to have an influence on the performance of the Li–S system [3]. Moreover, we tested the addition of graphitized carbon nanofibres (GCNF) for improving the electrode's electronic and thermal conductivity.

Three different types of sulphur with different particle size were investigated: sublimed, refined and precipitated. In Fig. 5, one can see SEM micrographs showing morphologies of electrodes made using these three different sulphurs. It is obvious that sublimed

sulphur contains the largest sulphur particles, while refined and precipitated sulphur particles appear to be of similar size (but with slightly larger particles in precipitated sulphur). However, the precipitated-sulphur particles visible in Fig. 5 are agglomerates and the primary particles of refined sulphur are actually larger.

In Fig. 6, the electrochemical performance of all three types of sulphur is presented. Despite the large differences in sulphur-particle size, one can see that the performance of all three electrodes is surprisingly similar. Precipitated sulphur seems to perform slightly better in cells without additive, however not significantly enough to allow drawing a definite conclusion. At the same time, when $LiNO_3$ is present in the electrolyte, after 100 cycles the best performing electrode seems to be the one with sublimed sulphur (with the largest S particle size); but again the effect is not significant enough to allow conclusively distinguishing its performance from others. The reason why the type and the particle size of the sulphur have no clear effect on the performance of the Li–S cells might be the working mechanism of Li–S batteries: upon lithiation solid sulphur is converted into the soluble polysulphides and a cycling rate of C/5 seems to be slow enough to allow even big particles to react. The carbon distribution in the electrodes after cycling would be different at macroscopic level, but there would be no changes on the microscopic level—therefore electrodes from different sulphur sources with different particle sizes perform similarly. A definite beneficial effect of $LiNO_3$ is that the coulombic efficiency is virtually 100%, while the practical specific charge after 100 cycles is at the same level of 700 mA h g^{-1} as in the case of electrolyte without additive.

In the next step, we have investigated the effect of a conductive additive different from Super P to the electrode; namely, we introduced graphitized carbon nanofibres (GCNFs), as they have shown good performance with other poorly conductive active materials, such as Si [17]. Sulphur–carbon composite electrodes containing GCNF have a completely different morphology than standard S–C electrodes, where the carbon component is only Super P (see Fig. 5). The whole electrode is permeated by GCNFs and has a more porous open structure (Fig. 7).

When GCNFs are added to the electrode formulations, replacing part of the Super P conductive additive (1/3 of Super P is replaced by GCNFs), better cycling stability can be observed (see Fig. 8). However, while the specific charge was more stable, it was lower than in composite S–C electrodes without GCNFs. The effect of the electrolyte amount is strongly pronounced in the system with the GCNF-containing electrode, as seen above also for electrodes without GCNF, especially when no additive is present in electrolyte (Fig. 1 and Fig. 8a). When $LiNO_3$ is added to the electrolyte, the specific charge values for both amounts of electrolyte are the same
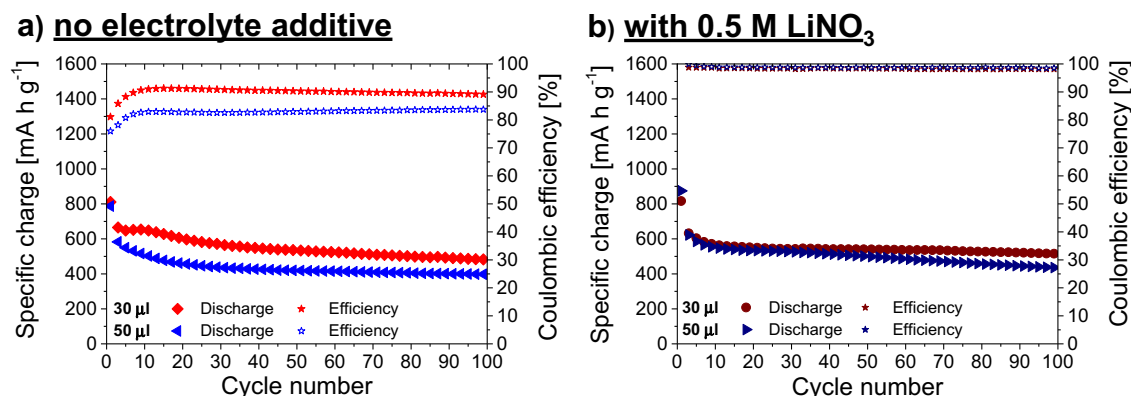

Fig. 8. Galvanostatic cycling of S–Super P/GCNF–PEO composite electrodes at C/5 rate with different amounts of electrolyte with no electrolyte additive (a) or with 0.5 M LiNO₃ (b).
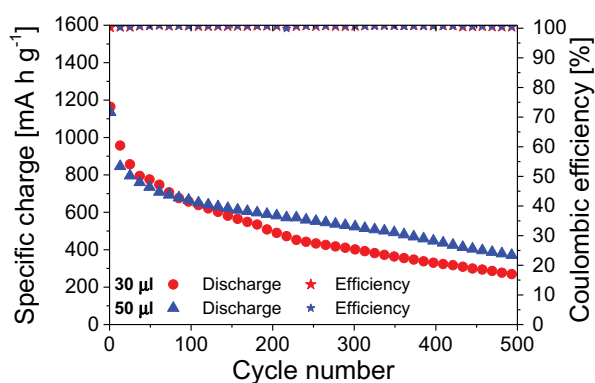
Fig. 9. Long-term cycling (500 cycles) using a standard S–C composite electrode (with 0.5 M LiNO$_3$ added to the electrolyte), cycled at a C/10 rate.

at the beginning of the cycling, but after 30–40 cycles; fading effect becomes more pronounced when cycling with the higher amount of electrolyte (Fig. 8b).

When testing different types of sulphur and GCNF as electrode conductive additive, LiNO$_3$ has been introduced as an electrolyte additive, but no enhanced performance in the form of higher specific charge was seen (see Figs. 6 and 8), despite positive effects reported in literature [18]. This may be due to the fact that LiNO$_3$ concentrations and amounts of electrolyte are different than reported in Ref. [18]. There are thorough and detailed studies on the effects of LiNO$_3$ presence in electrolyte [18,19], which conclude that it passivates the surface of metallic Li by creating a film and that the reaction after initial passivation is slow [19]. The LiNO$_3$ can have also a detrimental effect on the performance of the Li–S battery—it can be reduced irreversibly on the cathode side and grow endlessly on the anode side, consuming LiNO$_3$, according to the work of S. S. Zhang [20] (which contradicts work reported in ref. 19). However, the former process happens only at potentials below 1.6 V, which in turn does not explain the lower specific charges obtained in this work, where the cycling window is 1.8–2.7 V.

Most importantly, the usage of LiNO$_3$ as an electrolyte additive makes coulombic efficiency always increase, and at higher concentrations up to virtually 100%, independently of the value of the specific charge delivered by the composite electrode. Therefore, we conclude that addition of LiNO$_3$ should be avoided in situations where a positive effect of composite or carbon matrices needs to be established, as achieved high coulombic efficiency while using LiNO$_3$ does not necessary imply a better containment of sulphur species due to specific structure of carbon hosts for sulphur.

Long-term cycling is rarely shown in the literature dealing with Li–S batteries, and often it is considered to be impossible, especially with low amounts of electrolyte. It has been reported that the electrolyte is used up during cycling because of the increasing roughness of the lithium surface [2], necessitating an excess of electrolyte. Here we demonstrate 500 cycles at a slow C/10 rate and little electrolyte, 30 and 50 μl (Fig. 9). The specific charge fades greatly over 500 cycles and just after 100 cycles, the specific charge of the cell containing less electrolyte becomes lower than that with higher amount of electrolyte. Therefore effect of some parameters, when displaying and comparing only 100 or less cycles, can be misleading. Nonetheless, it has not been demonstrated before that long-term cycling of Li–S cells based only on physical mixture of commercially available S and C is possible, but been shown only recently for a special sulphur–TiO$_2$ yolk–shell nanoarchitecture

[21], which had fairly stable specific charge for 1000 cycles with remaining specific charge of ~700 mA h g^{-1}. The only other example is reported by L. Xiao et al. [22] on SPANI-NT/S (sulphur-polyaniline-nanotubes/sulphur)composite electrode, where after 500 cycles at 1C remaining specific charge was 400 mA h g^{-1}, same as our composites based on premixing commercially available cheap materials cycled at C/10 after the same amount of cycles.

4. Conclusions

In this study we have identified a number of experimental parameters that strongly influence the performance of Li–S test batteries. We urge that these parameters are routinely disclosed in the scientific literature when reporting results on the Li–S system, to enable comparison and reproduction. The amount of electrolyte, the presence of electrolyte additives and the salt concentration are the most crucial and influential factors. Other parameters, which are previously claimed to have a high impact on performance—among them sulphur-particle size, binder type and the presence of conductive additives to the electrode—did not significantly influence the performance results of our Li–S cells. In summary, our findings suggest that parameters related to the electrolyte have a more important role than those concerning electrode itself.

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